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J. Anal. Appl. Pyrolysis 81 (2008) 167–172
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
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Analytical pyrolysis as a direct method to determine the lignin content in wood
Part 2: Evaluation of the common model and the influence of compression wood

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Received 30 August 2007; accepted 4 November 2007
Available online 21 December 2007

Abstract

In Part 1, a method for the quantification of the lignin content (Py-lignin) of Maritime pine and spruce wood samples directly from the pyrograms was presented (A. Alves, M. Schwanninger, H. Pereira, J. Rodrigues, J. Anal. Appl. Pyrol. 76 (2006a) 209). The good correlation found between the Py-lignin and Klason lignin content gave a common model to both species.

In this work different larch species (*Larix* sp.) as well as varieties of European larch were used to evaluate this common model, revealing only small differences between the measured and the predicted Klason lignin contents. Compression wood was included due to the difference in lignin composition and content compared to normal wood. As the influence of compression wood was small a so-called "softwood model" including all samples was calculated (Py-lignin = 0.7325 × Klason lignin + 3.9195, $R^2 = 0.94$).

This can be used for pine, larch, and spruce wood with the limitation of the highest and lowest values where the species-specific models lead to better results, although more than 95% of the differences between the species-specific models and the "softwood model" lie within ±0.3%. It is expected that this model can predict the Klason lignin content of other softwoods.
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Keywords: Analytical pyrolysis; Compression wood; Klason lignin; *Larix* sp.; *Pinus pinaster*; *Picea abies*; Py-lignin

1. Introduction

Analytical pyrolysis is being increasingly used as a quantitative method in the wood and pulp field to assess chemical composition of lignocellulosic materials [1–4]. The main advantages of analytical pyrolysis over classical wet-chemical methods are an easy sample preparation (drying and milling), rapid analysis times and small sample sizes required (μg range) [5]. Analytical pyrolysis data were related with classical wet-chemical data by direct comparison of peak areas of characteristic pyrolysis products [6–9], calibration using multivariate techniques [10,11], and absolute quantification of pyrolysis products using internal standards [12–14].

In Part 1, a method for the quantification of the lignin content (Py-lignin) of Maritime pine and spruce wood samples directly from the pyrograms was presented [1]. Good correlation was found between the Py-lignin and Klason lignin content for each species as well as a good common model to both species. In this work, the Py-lignin content of larch wood samples with known Klason lignin content was determined, which was further used to evaluate this common model. It was hypothesized that this

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doi:10.1016/j.jaap.2007.11.001

common model that includes pine and spruce wood is also valid for other softwoods such as larch. Thereafter a ‘‘softwood model’’ including larch wood was calculated. Furthermore, the influence of so-called compression wood, a type of reaction wood formed under mechanical stresses [15], was assessed on the basis of existing differences in lignin composition and content, as compared to normal wood.

2. Experimental

The pine and spruce wood samples as well as the analytical pyrolysis analysis were previously described [1].

2.1. Sampling

2.1.1. Larch wood samples

A comprehensive sample set of mostly European larch (*Larix decidua*) varieties, of hybrid larch (*Larix eurolepis*) and of Japanese larch (*Larix kaempferi*) was used. Most trees were harvested at an age of 38, however, old-growth larch trees from high elevation were also included. Sampling sites are spread across Europe, further details of the 21 samples are given in Table 1; about sample preparation and processing in [16–19].

2.1.2. Spruce wood samples

One 30-year-old Norway spruce tree (*Picea abies* [L.] Karst) from Austria was harvested and a sample prepared as described by Gindl [20]. The compression wood of this tree with known Klason lignin content [20] was used in the study.

Additionally one wood sample containing compression wood from a 19-year-old spruce tree (*P. abies* (L.) Karst) from Sweden, with a Klason lignin content of 32.1%, based on oven-dry mass of extractive-free material was used [21].

The sample preparation of the extractives-free material prior analytical pyrolysis can be found in Part 1 [1].

2.2. Statistics

The root mean square error of prediction (RMSEP) was calculated as follows:

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n}(K_{\mathrm{pred}_i} - K_{\mathrm{meas}_i})^2}{n}},$$

where n is the number of samples, K_{pred} is the Klason lignin content predicted with the common model, and K_{meas} is the measured Klason lignin content.

3. Results and discussion

3.1. Evaluation of a Py-lignin model based on pine and spruce

As shown in Part 1 [1] analytical pyrolysis can be used to predict the lignin content of pine and spruce wood. A good correlation was obtained between Py-lignin and Klason lignin content. It was anticipated that a model using both, pine and spruce wood, could also be valid for other softwood species, which was tested here with larch.

This common model obtained by combining the results of pine and spruce, as reported in Part 1 [1], ($R^2 = 0.93$ and Py-lignin = 0.7286 × Klason lignin + 4.0132; Fig. 1) was taken to predict Klason lignin content.

To evaluate this model 21 larch wood samples with known Klason lignin content (Table 1) were assessed by analytical pyrolysis according to Alves et al. [1]. The Klason lignin content

Table 1
Site, origin, species, age, Klason lignin and Py-lignin content (% extractive-free o.d.w.) of the larch wood samples

Sample	Origin	Growth site	Species-variety	Age	CW	Klason lignin (%)	Py-lignin (%)
342exf	Blizyn (PL)	Elm (DE)	*L. decidua polonica*	38	No	27.6	24.4
343exf	Blizyn (PL)	Elm (DE)	*L. decidua polonica*	38	No	30.7	26.1
326exf	Blizyn (PL)	Elm (DE)	*L. decidua polonica*	38	Low	30.1	25.5
035exf	Hybrid	Clanna (GB)	*L. x eurolepis*	39	Low	29.5	25.4
084exf	Hybrid	Coat-An-Noz (FR)	*L. x eurolepis*	38	Low	30.4	26
056exf	Hybrid	Coat-An-Noz (FR)	*L. x eurolepis*	38	Low	30.9	26.4
352exf	Ina (JP)	Coat-An-Noz (FR)	*L. kaempferi*	38	Low	30.1	25.4
160exf	Langau (AT)	Langau (AT)	*L. decidua alpica*	160	No	28.4	24.8
168exf	Langau (AT)	Langau (AT)	*L. decidua alpica*	160	No	29.1	25.2
235exf	Langau (AT)	Nassogne (AT)	*L. decidua alpica*	38	Low	26.6	23.6
151exf	Langau (AT)	Langau (AT)	*L. decidua alpica*	160	Low	28	24.3
221exf	Montgenevre (FR)	Coat-An-Noz (FR)	*L. decidua alpica*	38	No	28.1	24.7
222exf	Montgenevre (FR)	Coat-An-Noz (FR)	*L. decidua alpica*	38	High	26.8	24.2
217exf	Montgenevre (FR)	Coat-An-Noz (FR)	*L. decidua alpica*	38	High	27.2	24
255exf	Ruda (PL)	Nassogne (BE)	*L. decidua sudetica*	38	No	29.1	25.2
194exf	Ruda (PL)	Elm (DE)	*L. decidua sudetica*	38	No	32	27.2
192exf	Ruda (PL)	Elm (DE)	*L. decidua sudetica*	38	High	29.8	26
321exf	Zabreh (CZ)	Coat-An-Noz (FR)	*L. decidua sudetica*	38	No	27.2	24.2
288exf	Zabreh (CZ)	Nassogne (BE)	*L. decidua sudetica*	38	No	28.6	25.1
285exf	Zabreh (CZ)	Nassogne (BE)	*L. decidua sudetica*	38	Low	28.8	25.6
292exf	Zabreh (CZ)	Nassogne (BE)	*L. decidua sudetica*	38	High	31.6	26.7

CW, compression wood content; exf, extractives-free. Country codes: AT, Austria; BE, Belgium; CZ, Czech Republic; DE, Germany; FR, France; GB, United Kingdom; JP, Japan; PL, Poland.

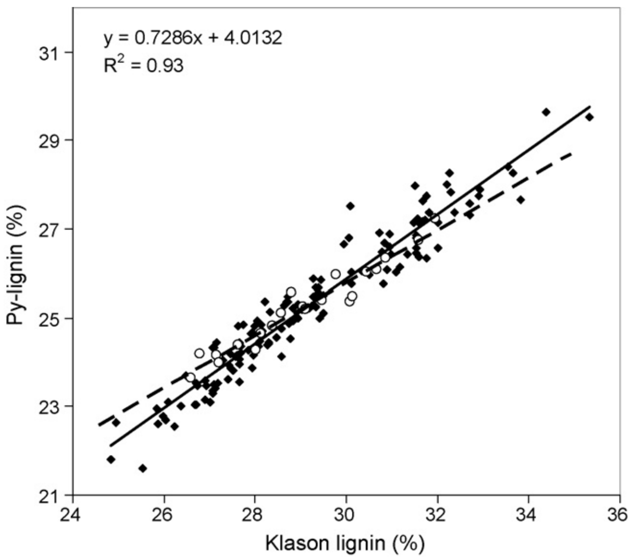

Fig. 1. Py-lignin versus Klason lignin content of pine and spruce samples (closed diamonds). The 21 larch samples are displayed with open circles. The broken line is the tendence line.

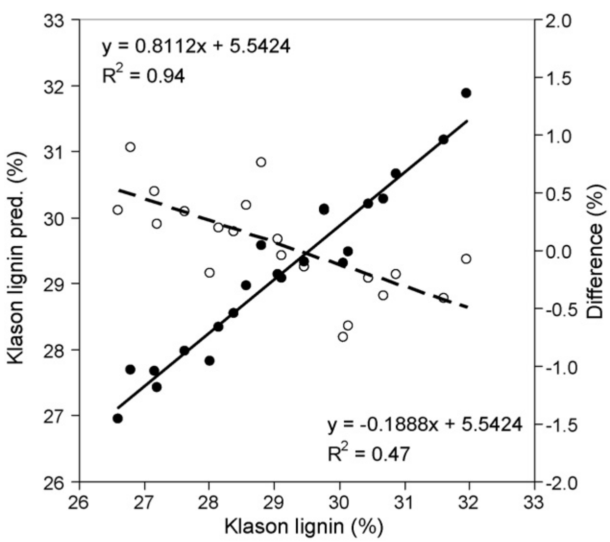

Fig. 2. Klason lignin content of Larch wood predicted with the common model (pine and spruce) versus Klason lignin (filled circles). Differences between predicted and the measured Klason lignin content versus Klason lignin content (open circles).

predicted with the obtained Py-lignin was compared to the measured Klason lignin content (Fig. 2). A good correlation with an R^2 of 0.94 and a slope of 0.8112 was obtained. It is known that Py-lignin increasingly underestimates the Klason lignin content [1] as the values get higher, a slope deviation from one was therefore expected. The slope (0.8112) possibly indicates a deviation of the regression between Py-lignin and Klason lignin of larch wood samples from the one used for prediction.

The differences between predicted and measured Klason lignin content, and the Klason lignin content are negatively correlated (Fig. 2). This was expected due to the lower slope of the tendence line for the larch wood samples compared to the regression line of the common model (Fig. 1).

The root mean square error of prediction of 0.42% is close to the stated repeatability of the Klason lignin TAPPI standard method [22], and 85% of the predicted values lie within ±RMSEP. The standard deviation expressed as a percentage of the mean is 1.45%.

A linear regression model with all samples (pine, spruce and larch), further on called model A, showed almost the same results ($R^2 = 0.93$ and Py-lignin = 0.7188 × Klason lignin + 4.3045; Fig. 3). The larch wood samples are closely positioned to the regression line (Fig. 3, open circles).

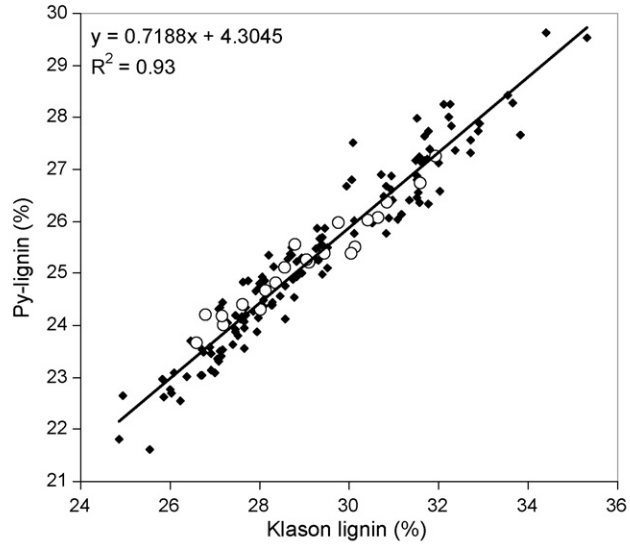

Fig. 3. Py-lignin versus Klason lignin content of pine, spruce, and larch samples. The larch samples are displayed with open circles.

3.2. Influence of compression wood

Two spruce samples with compression wood with known Klason lignin content were accessed by analytical pyrolysis and the Klason lignin contents estimated using Py-lignin results and

Table 2
Klason lignin content of two spruce compression wood samples (CW) measured and predicted by the spruce model and model A

Sample	Py-lignin (%)	Klason lignin (%)				
		Measured	Spruce model Py = 0.8606 × Kla + 0.373		Model A Py = 0.7188 × Kla + 4.3045	
			Predicted	Difference	Predicted	Difference
CW1	31.7	37.2	36.4	−0.7	38.1	1.0
CW2	28.3	32.1	32.4	0.3	33.3	1.2

Py, Py-lignin; Kla, Klason lignin.

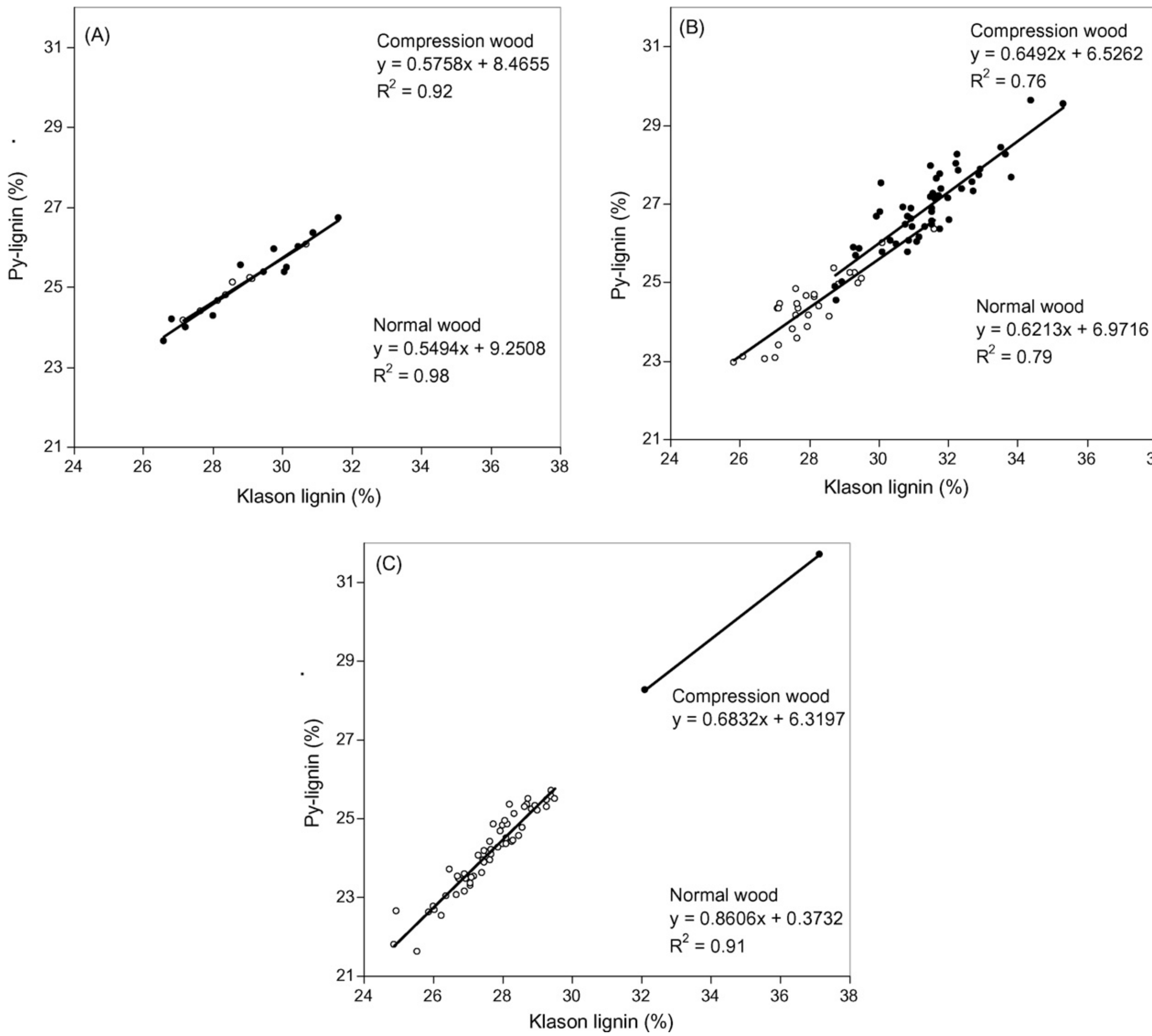

Fig. 4. Py-lignin versus Klason lignin content of larch (A), pine (B), and spruce (C) samples. Normal wood samples are displayed with open circles, compression wood samples with closed circles.

the spruce model [1] as well as the model A (Table 2). The differences between predicted and measured Klason lignin content are smaller for the spruce model than for the model A (Table 2). Since the spruce model does not contain compression wood (CW) samples and the model A contain samples with and without compression wood it was needed to investigate the influence of CW on the correlation between Py-lignin and Klason lignin. The pine and larch data sets were divided in normal wood (NW) and compression wood (Fig. 4).

The main differences were observed in the slope of the linear regression lines between spruce and the other two species. For larch almost identical regression lines were obtained for CW and NW (Fig. 4A). For pine almost identical slopes were obtained for CW and NW with a small shift between them (Fig. 4B). No explanation was found for this shift. Spruce NW slope line shows the highest slope (0.86). The sloping line of spruce CW (Fig. 4C) although only obtained with two samples with high compression wood was closer to the CW slopes of pine and larch.

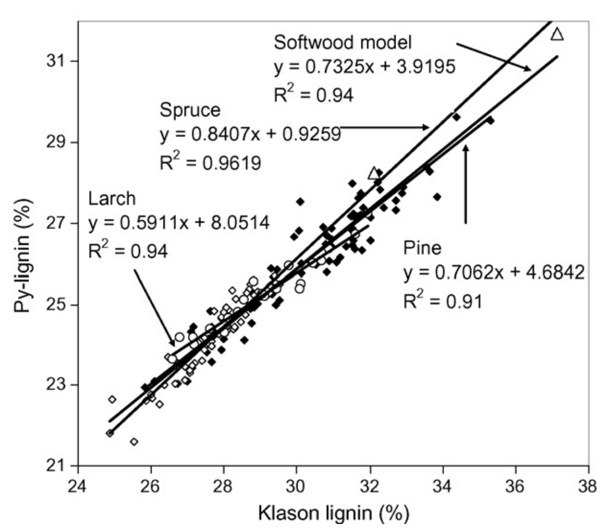

Fig. 5. Py-lignin versus Klason lignin content of larch (open circles), pine (closed diamonds), spruce (open circles) samples, and of all samples (''softwood model''). The two spruce CW samples are displayed with open triangles.

By adding the two CW samples (Fig. 5, triangles) to the spruce model only a small decrease in the slope from 0.86 to 0.84 was obtained (Fig. 5). This confirms the findings for pine and larch that CW and NW samples lies close to the species-specific regression lines.

The two CW samples were included and a ‘‘softwood model’’ calculated and compared with the species-specific models. The distribution of differences between the Klason lignin contents predicted with species-specific models and the ‘‘softwood model’’, as well as the distribution of differences between the Py-lignin contents predicted with species-specific models and the ‘‘softwood model’’ is shown in Fig. 6. Both show an approximately normal distribution. More than 95% of the differences lie within ±0.3%. This means that the softwood model can be used for the prediction of the Klason lignin content instead of the species-specific models. Only the spruce and larch samples with the lowest and the highest Klason lignin contents fell out of this range (±0.3%). These samples can be predicted more precisely by species-specific models.

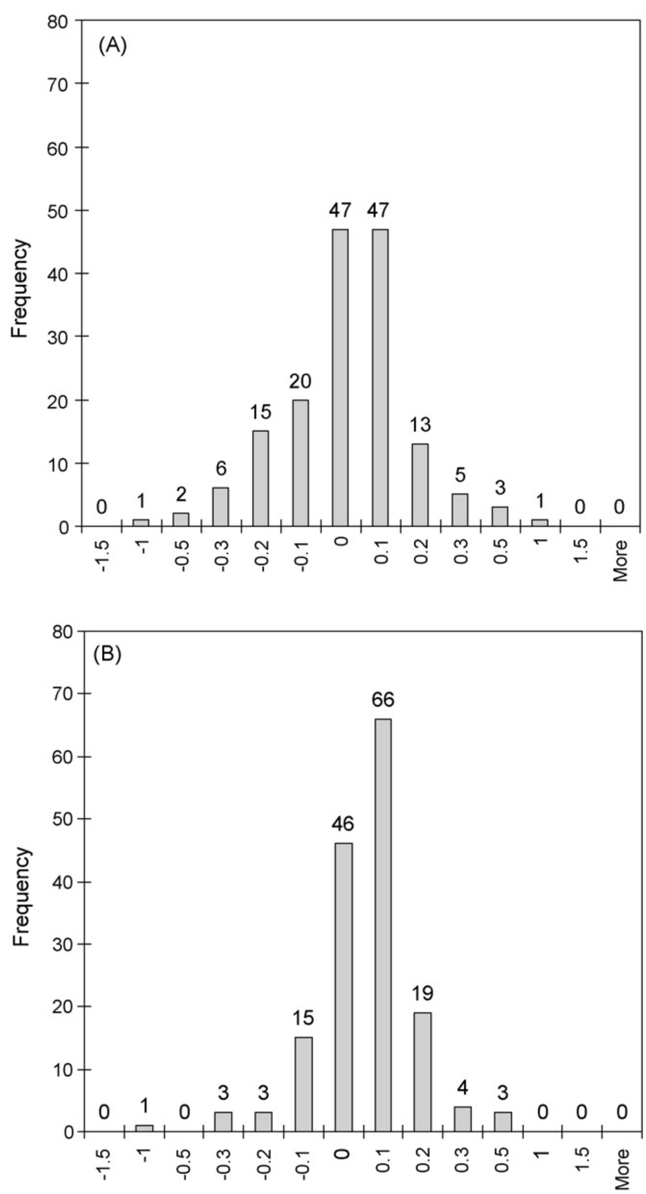

Fig. 6. (A) Distribution of differences between the Klason lignin contents predicted with species-specific models and the ‘‘softwood model’’, and (B) distribution of differences between the Py-lignin contents predicted with species-specific models and the ‘‘softwood model’’.

The slightly different slopes of the linear regression lines of pine and larch, and especially the one of spruce (Fig. 5) suggest possible differences in lignin and/or carbohydrate composition that should be investigated.

4. Conclusions

The evaluation of a Py-lignin model based on pine and spruce wood with larch wood samples revealed only small differences between the measured and the predicted Klason lignin contents of larch. Therefore, larch samples could be included in the model. The investigation of the influence of compression wood revealed small differences between normal wood and compression wood, with a so far unexplained shift between NW and CW within pine wood. Although, the slope of the spruce model was much higher compared to pine and larch, the spruce samples could be predicted well in general. Therefore, this so-called ‘‘softwood model’’ can be used for pine, larch, and spruce wood with the limitation of the highest and lowest values where the species-specific models have led to better results. Moreover, it is expected that this model can also be used to predict Klason lignin contents of other softwood species.

Acknowledgements

The work was financially supported by Fundação para a Ciência e Tecnologia (Portugal), research projects (POCTI/AGR/47353/2002 and PTDC/AGR-CFL/72606/2006) and the grant holder of first author SFRH/BD/28679/2006. This research is included in the activities of BIOPOL in Centro de Estudos Florestais (Portugal). We acknowledge the benefit of obtaining samples from the EU-project ‘‘Towards a European Larch Wood Chain (FAIR 98–3354)’’. We thank Wolfgang Gindl for providing the two spruce samples.

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